PTO 03-2661

Japanese Kokai Patent Application
No. Hei 8[1992]-213341

A METHOD FOR THE MANUFACTURE OF CROSSLNKED OLEFIN RESIN FOAM

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UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. APRIL 2003
TRANSLATED BY THE RALPH MCELROY TRANSLATION COMPANY

JAPANESE PATENT OFFICE
PATENT JOURNAL (A)
KOKAI PATENT APPLICATION NO. HEI 8[1992]-213341

Int. Cl.^{5}:	C 08 J 9/06 //C 08 L 23:00
Sequence No. for Office Use:	8927-4F
Filing No.:	Hei 8[1991]-7787
Filing Date:	January 25, 1991
Publication Date:	August 4, 1992
Priority Date: Country: No.:	 April 11, 1990 JP Hei 8[1990]-97291
No. of Claims:	2 (Total of 6 pages)
Examination Request:	Not filed

A METHOD FOR THE MANUFACTURE OF CROSSLINKED OLEFIN RESIN FOAM

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[There are no amendments to this patent.]

Claims

1. A method for the manufacture of crosslinked olefin resin foam, characterized in that an olefin resin composition sheet containing an organic peroxide and thermal decomposition type foaming agent is surface-crosslinked by irradiating low-voltage electron beam of 50-400 keV then heated for chemical crosslinking by the organic peroxide and decomposition foaming by the thermal decomposition type foaming agent.

2. The manufacturing method described in Claim 1, wherein the electron beam irradiation is carried out in an atmosphere of low oxygen concentration.

Detailed explanation of the invention

[0001]

Industrial application field

The present invention concerns crosslinked olefin resin foams, and more specifically concerns a highly productive method for the manufacture of crosslinked olefin resin foams with smooth beautiful appearances.

[0002]

Prior art

Usually, crosslinked olefin resin foams are manufactured by foaming after forming crosslink bonds in the resin for improved viscoelastic flow characteristics. Methods for the manufacture of crosslinked olefin resin foams can be divided according to crosslinking processes for generating crosslink bonds, more specifically, (1) crosslinking by generation of radicals in olefin resin molecules by irradiation of ionizing radiation; (2) chemical radical crosslinking by formation of radicals by decomposition of organic peroxides, abstraction of hydrogen from the olefin resin by the radicals to form radicals in the resin for crosslinking; (3) chemical condensation crosslinking by forming a molding from a foamable resin composition using an alkoxy group-containing silicon compound-grafted or copolymerized resin, then dehydration and condensation of alkoxy group for crosslinking, etc.

[0003]

However, these methods have following advantages as well as problems.

(1) In the crosslinking by ionizing radiation, ionizing radiation is irradiated before foaming to impart a certain degree of crosslinking (usually 15-45% in terms of gel fraction) to the resin to obtain the viscoelasticity needed for pore formation in the resin during the foaming to obtain foams having a relatively uniform degree of crosslinking in the thickness direction, pore uniformity a and smooth beautiful surface. However, with the increasing degree of crosslinking, excessive viscoelasticity of the resin may prevent sufficient expansion, cause surface cracks, cause the degree of crosslinking to be reduced, and the resulting foams may have poor heat resistance. Also, the ionizing radiation has rather limited penetrating power into foamable resin composition sheets, thus with this method, foams with a substantial thickness cannot be obtained.

[0004]

(2) In the crosslinking by organic peroxides, the crosslinking reaction proceeds before, during and after foaming, enabling a relatively high degree of crosslinking, giving foams with excellent heat resistance. Furthermore, thick foams can be obtained. However, since the surface of the foamable resin composition sheet is exposed to oxygen at high temperature, oxygen molecules may bond to the resin radical formed by the hydrogen abstraction reaction by the radical formed by decomposition of organic peroxide, negating the crosslinking reaction activity or resulting in oxidative decomposition of the resin or lowering of the organic peroxide decomposition radical activity. As a result, crosslinking does not proceed at all in the surface of the foamable resin composition sheet, and pores in the surface layer are broken during foaming, resulting in foams with coarse surface.

[0005]

(3) In the crosslinking by alkoxysilane, the crosslinking is by condensation reaction, thus there is no effect of oxygen and the crosslinking proceeds to the surface layer, giving foams of smooth surface. Also, thick products can be produced. However, preparation of alkoxysilane-grafted or copolymerized resins is necessary, and the crosslinking also requires lengthy treatment with hot water or steam. Thus, the process is complicated and special facilities are needed, which is not advantageous for productivity and production cost.

[0006]

There are also other methods of using both ionizing radiation and organic peroxides for crosslinking of olefin resin composition sheets as disclosed in Japanese Kokoku Patent No. Sho 45[1970]-28503 and Japanese Kokai Patent Application No. Sho 62[1987]-250039 for improved heat resistance, moldability, appearances, etc.

[0007]

In the above methods, while radicals are formed in the olefin resins by hydrogen abstraction by the ionizing radiation energy, they may bond with the organic peroxide decomposition radicals, resulting in significantly reduced crosslinking efficiency. Therefore, in conventional methods, in the case of relatively high-voltage ionizing radiation irradiation and using a large amount of organic peroxide, such reactions may occur competitively, and crosslinking needed for foaming may not occur. On the other hand, when the amount of organic peroxide used is too small, decomposition may occur during irradiation, resulting in reduced crosslinking during or after crosslinking, and thus a high degree of crosslinking is difficult to

obtain. Therefore, competitive reactions and reaction activity cancel each other at and the desired effects cannot be obtained. It is difficult to use these methods in actual production.

[0008]

More recently, an olefin resin sheet containing a foaming agent and chemical crosslinking agent is laminated with a polyolefin resin composition sheet containing a foaming agent, then the surface layer is irradiated with ionizing radiation, followed by thermal foaming of the entirety (Japanese Kokai Patent Application No. Hei 8[1989]-286826). This process combines advantages of radiation crosslinking and chemical radical crosslinking to obtain foams with smooth appearances. However, this process requires lamination of different foamable resin composition sheets, and making each sheet by different processes and coextrusion lamination requires complex heavy facilities. Furthermore, lamination has to be done at a relatively low temperature that is below the decomposition temperatures of foaming agent and crosslinking agent, thus the lamination interface may not become one piece and the layers may separate during foaming with formation of large pores between the layers.

[0009]

Problems to be solved by the invention

It is an object of the present invention to overcome the problems of the prior art to provide a method for the manufacture of crosslinked olefin resin foams with excellent appearance and properties. Namely, it is an object of the present invention to provide foams with no surface pore breakage and with smooth beautiful appearances. It is also an object of the present invention to provide a method for the manufacture of crosslinked olefin resin foams with qualities needed for various applications with the degree of crosslinking ranging from low to high degree (for example, foams with a low degree of crosslinking have good stretchability during thermal processing, and foams of high degree of crosslinking have good heat resistance). Also, it is an object of the present invention to provide a method for the manufacture of crosslinked olefin resin foams of a substantial thickness. It is an another object of the present invention to provide a method for the manufacture of crosslinked olefin resin foams with high productivity without complex processes and facilities.

[0010]

As a result of an intense investigation, we have discovered that the objectives can be achieved by irradiating olefin resin composition sheets containing organic peroxides and thermal decomposition type foaming agents with an electron beam of acceleration voltage that is lower

than that used in the prior art, then thermal foaming with chemical crosslinking by the organic peroxides and foaming by the thermal decomposition type foaming agents.

[0011]

Namely, with irradiation of a low-voltage electron beam of 50-400 keV, the electron beam penetration is only near the surface layer. Thus, by the low-voltage electron beam irradiation, the organic peroxide in the surface layer is decomposed and its activity is eliminated. With irradiation of both sides of the sheet with relatively high dosage (desirably 1-10 Mrad) needed for crosslinking the olefin resin, the degree of crosslinking (usually 10-40% in terms of gel fraction) for obtaining the viscoelasticity needed for foaming the surface layer is achieved, and pore breakage during the thermal foaming is prevented. Next, by thermal foaming, the inner layer portion occupying most of the thickness of foam is subjected to crosslinking by the organic peroxide without effect of electron beam irradiation, resulting in a foam with smooth beautiful appearances and excellent properties.

[0012]

However, during the electron beam irradiation, the surface of foamable resin composition sheet is exposed to oxygen, thus the polyolefin radical formed by electron beam induces decomposition of the organic peroxide, and the resulting peroxide radical bonds with the oxygen in air. As a result, polyolefin crosslinking does not proceed further, and sufficient surface smoothness may not be obtained. Here, foams with excellent surface smoothness and good properties can be obtained in stable manner by carrying out the electron beam irradiation in an atmosphere of low oxygen concentration.

[0013]

The present invention is achieved based on such a discovery.

[0014]

Means to solve the problems

The present invention provides a method for the manufacture of crosslinked olefin resin foams, characterized in that an olefin resin composition sheet containing an organic peroxide and thermal decomposition type foaming agent is surface-crosslinked by irradiating a low-voltage electron beam of 50-400 keV, then heated for chemical crosslinking by the organic peroxide and decomposition foaming by the thermal decomposition type foaming agent. In the present invention, it is preferred to carry out the electron beam irradiation in an atmosphere of low oxygen concentration, such as inert gas. Next, the present invention is explained in detail.

[0015]

Crosslinking and foaming

In the present invention, first, a foamable olefin resin composition sheet containing an organic peroxide and thermal decomposition type foaming agent is irradiated with low-voltage electron beam of 50-400 keV, preferably 100-300 keV. By such low-voltage electron beam irradiation, the organic peroxide present in the surface layer is decomposed, losing its activity, and then both sides of the sheet are irradiated at relatively high dosage to cause desirable crosslinking of the olefin resin in the surface layer. The dosage may vary according to the type of olefin resins used, while it is usually 1-10 Mrad, preferably 2-6 Mrad.

[0016]

It is preferred to carry out the electron beam irradiation in an atmosphere of low oxygen concentration, especially an oxygen concentration below 1000 ppm, preferably below 400 ppm. For low oxygen concentration, usually, an inert gas is introduced into the electron beam irradiation region. The inert gas may be nitrogen, helium, argon, etc., while nitrogen gas is preferred in terms of cost. The polyolefin radical formed by low-voltage electron beam irradiation induces decomposition of the organic peroxide present in the surface layer to form peroxide radicals. However, in an atmosphere of low oxygen concentration, bonding of this radical with oxygen can be suppressed or prevented, and new hydrogen abstraction from the polyolefin resin generates olefin radicals. Thus, the crosslinking reaction proceeds.

[0017]

With an [appropriate] degree of crosslinking (10-40% in terms of gel fraction) for viscosity as required for foaming of the sheet surface layer, pore breakage during thermal foaming can be prevented. Next, foaming is achieved by heating for decomposition of the thermal decomposition type foaming agent. At this point, the organic peroxide is mostly in the interior of the sheet, and thus is not decomposed by the low-voltage electron beam irradiation with sufficient progress of the crosslinking reaction. As a result, foams of smooth beautiful surface are obtained with no pore breakage in the foam surface. Since the organic peroxide present inside the sheet is not affected by the low-voltage electron beam, the average degree of crosslinking of foams can be controlled by varying the type and amount of organic peroxide used.

[0018]

In this process, electron beam penetration needed is only in the surface portion, and penetration into the inner layer is not necessary, thus production of thick products is possible. Furthermore, since lamination of sheets of different compositions is not necessary, there is no bonding interface, thus interlayer separation and large pore formation do not occur at all during foaming. By carrying out electron beam crosslinking with prevention of surface layer pore breakage, the foamable resin composition sheet displays good shape retention even under heat, and even without pre-crosslinking [occurring] by partial decomposition of the organic peroxide before foaming, the sheet can be introduced directly into the foaming oven, with the foaming and organic peroxide crosslinking at the same time. Thus, this process is highly productive.

[0019]

In the process of the present invention, in the electron beam irradiation, the acceleration voltage is limited to 50-400 keV. Below 50 keV, the electron beam penetration depth is too shallow, and prevention of pore breakage in the surface layer is not sufficient. On the other hand, above 400 keV, the electron beam penetrates relatively deep inside of the resin composition sheet, and the degree of crosslinking elevation in the inner layer is interfered with by competition with the reaction and organic peroxide decomposition, thus 100-300 keV is preferred.

[0020]

The thickness of foamable olefin resin sheet is usually above 0.5 mm, preferably above 1 mm. The thickness of the surface layer to be crosslinked by the low-voltage electron beam irradiation is usually 0.1-0.5 mm, preferably 0.1-0.3 mm. In the case of sheets thinner than 0.5 mm, the organic peroxide is affected by electron beam throughout entire inner layer, and it is difficult to achieve the objectives.

[0021]

In the process of the present invention, such effects are further pronounced when non-aromatic organic peroxides having no benzene ring in the molecular structure are used instead of those with benzene rings that absorb electron beam energy.

[0022]

For hastening crosslinking during thermal foaming, preventing partial pore breakage in the foam inner layer and further enhancing pore stability and closed pore content, it is effective to use organic peroxides having decomposition half life of 1 min at 140-180°C and a small

amount, desirably less than 0.4 parts by weight, of organic peroxides of low decomposition temperature at 120-140°C.

[0023]

Olefin resins

The olefin resins that can be used in the present invention are, e.g., low-density polyethylene, medium to high-density polyethylene, linear low-density polyethylene, polypropylene, butane-propylene copolymer, ethylene-propylene copolymer, ethylene-vinyl acetate copolymer, vinyl chloride-ethylene copolymer, ethylene-acrylate copolymer, etc. They many be used individually or as mixtures thereof.

[0024]

Organic peroxides

Specific examples of organic peroxides that can be used in the present invention are those having decomposition half life of 1 min at the temperature shown below, such as 2,4-dichlorobenzoyl peroxide (121°C), benzoyl peroxide (130°C), 1,1-di(t-butylperoxy)-3,3,5-trimethylcyclohexane (148°C), n-butyl-4,4-di(t-butylperoxy)valerate (166°C), dicumyl peroxide (171°C), □□'-bis((t-butylperoxyisopropyl)benzene (175°C), 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3 (179°C), t-butylperoxycumene (176°C), etc.

[0025]

Such organic peroxides may be used individually or as mixtures thereof. Of these, especially effective are non-aromatic 1,1-di(t-butylperoxy)-3,3,5-trimethylcyclohexane, n-butyl-4,4-di(t-butylperoxy)valerate, 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3, etc., for low electron beam absorption by benzene ring. The amount of the organic peroxides added is usually 0.4-2.0 parts by weight, preferably 0.6-1.5 parts by weight to 100 parts by weight of the olefin resin.

[0026]

Thermal decomposition type foaming agents

The foaming agents are, e.g., azodicarbonamide, oxybisbenzenesulfonyl hydrazide, etc. which are thermal decomposition type foaming agents generating pores by thermal decomposition. The amount added can be varied according to degree of foaming desired, and in general, it is 2.5-25 parts by weight to 100 parts by weight of olefin resin.

[0027]

Other additives

If needed, the olefin resin compositions used in the present invention may contain foaming aids such as fatty acid metal salts, zinc flower, etc. for improving the decomposition properties of foaming agents, crosslinking aids such as trimethylolpropane trimethacrylate, divinylbenzene, etc., antioxidants, colorants, fire retardants, fillers, etc.

[0028]

Examples

Next, the present invention is explained in further detail with examples.

Measurement of physical properties

Degree of crosslinking

A small cut from foam is immersed in xylene at 120°C for 24 h, and the undissolved residue is vacuum dried at 80°C for 8 h and weighed. Ratio of this weight to initial foam weight is given as the degree of crosslinking.

[0029]

Appearances

The foam surface layer was observed visually and evaluated in 5 ranks as shown below.

◎: high excellence in smoothness and beauty

O: excellent smoothness and beauty

∈: good smoothness and beauty

X: poor smoothness with coarse surface

[0030]

<u>Application Examples 1-5, Comparative Examples 1-2</u>

In a Henshel mixer, 100 parts by weight of low-density polyethylene resin (MI: 2.5, density: 0.922), 15 parts by weight of azodicarbonamide foaming agent, 1.5 parts by weight of zinc flower foaming aid, and organic peroxide in an amount shown in Table 1 were mixed evenly, extruded through a T-die in a single-screw extruder of 65 mm□ (L/D = 26) to form a sheet of 3 mm thickness and 450 mm width. The temperature conditions of extruder were, from the compound inlet side, 130°C, 135°C, 140°C, with die temperature 125°C and extrusion rate 30 kg/h.

[0031]

Then, using a self-shield low-voltage small electron beam irradiator, the sheet was irradiated on both sides at the voltage and dosage given in Table I and placed in an oven at about 220°C to obtain a foam sheet of about 7 mm in thickness, about 800 mm in width and about 30-fold in foaming expansion. The electron beam irradiation was carried out in air. Results are given in Table I. For comparison, the crosslinking was done by organic peroxide without sheet surface irradiation or sheet was irradiated on both sides with high-voltage electron beam (800 keV).

[0032]

Table 1

			①実施例							比較例②
			1			2	3	4	5	1	2
③架橋剤	ジクミルペルオキシド④		0.6			0.8	1.5	—	—	0.8	0.8
	n-ブチル-4,4'-ジ(t-ブチルペルオキシ)バレレート⑤		—			—	—	0.5	0.5	—	—
	ベンゾイルペルオキシド⑥		—			—	—	—	0.1	—	—
⑦照射	電圧(keV)⑧		100	200	300	300	300	300	250	—	800
	線量(Mrad)⑨		8	4	4	4.5	5	4	4.5	—	2.5
⑩発泡体	架橋度(%)⑪	表層(0.5mm)⑫	14	23	28	23	21	30	32	10	—
		中心層⑬	32	38	33	44	63	33	37	42	7
	外観状況⑭		△	○	○	○	○	◎	◎	×	*

*Pore breakage throughout, foams not satisfactory

Key:
1 Application Example
2 Comparative Example
3 Crosslinking agent
4 Dicumyl peroxide
5 n-butyl-4,4'-di(t-butylperoxy)valerate
6 Benzoyl peroxide
7 Irradiation
8 Voltage
9 Dosage
10 Foams
11 Degree of crosslinking
12 Surface layer

13 Core layer
14 Appearances

[0033]

Application Examples 6-11, Comparative Example 3

In a Henshel mixer, 100 parts by weight of low-density polyethylene resin (MI: 2.5, density: 0.922), 15 parts by weight of azodicarbonamide foaming agent, 1.5 parts by weight of zinc flower foaming aid, and organic peroxide (dicumyl peroxide) in an amount shown in Table 2 were mixed evenly, extruded through a T-die in a single-screw extruder of 65 mm (L/D = 26) to form a sheet of 2 mm in thickness and 450 mm in width. The temperature conditions of extruder were, from the compound inlet side, 130°C, 135°C, 140°C, with die temperature 125°C and extrusion rate 30 kg/h.

[0034]

Then, using a self-shielding low-voltage small electron beam irradiator, the sheet was irradiated on both sides in a nitrogen atmosphere (oxygen concentration: 200 ppm) at a voltage of 200 keV and the dosage given in Table 2 and placed in an oven at about 230°C to obtain a foam sheet of about 7 mm thickness, about 800 mm width and about 30-fold in foaming expansion. The electron beam irradiation was carried out in air. Results are given in Table 2.

[0035]

In the case of electron beam irradiation in air, for comparison, the crosslinking was done by organic peroxide without sheet surface irradiation. Results are given in Table 2.

[0036]

Table 2

			① 実施例						比較例 ②
			6	7	8	9	10	11	3
			窒素中照射 ③				空気中照射 ④		–
⑤ 照射	電圧 (kev) ⑥		200	200	200	200	200	200	200
	線量 (Mrad) ⑦		4	4	4	5	4	5	–
⑧ ジクミルペルオキシド			0.2	0.4	0.6	0.8	0.8	0.8	0.6
⑨ 発泡体	架橋度 (%) ⑩	表層 (0.5mm) ⑪	43	38	35	30	24	22	8.9
		中心層 ⑫	44	54	59	54	40	35	63
	外観状況 ⑬		◎	◎	◎	◎	○	△	×

Key:
1 Application Example
2 Comparative Example
3 Irradiation in nitrogen
4 Irradiation in air
5 Irradiation
6 Voltage
7 Dosage
8 Dicumyl peroxide
9 Foams
10 Degree of crosslinking
11 Surface layer
12 Core layer
13 Appearances

[0037]

Effect of the invention

According to the present invention, smooth beautiful foams can be obtained without crosslinking for prevention of surface pore breakage prior to foaming.

[0038]

Also, according to the method of the present invention, the electron beam affects only the surface layer of the sheet and has no effect on the organic peroxide in the inner layer, thus the

degree of crosslinking can be raised by increasing the organic peroxide concentration in the inner layer to satisfy the heat resistance required for [many] applications. Also, electron beam penetration into inner layer is not necessary, so that thick products can be produced.

[0039]

Furthermore, after low-voltage electron beam irradiation on the surface layer, sheets can be heated directly in a foaming oven for crosslinking by organic peroxide and foaming by the thermal decomposition type foaming agent, thus productivity is excellent.